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Techniques for the Estimation of Heats of Explosion (HEX) Using Thermochemical Codes

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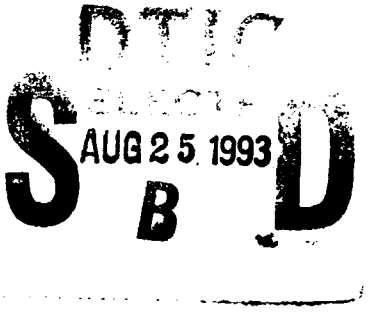

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Procedures are outlined for calculating the heats of explosion (HEX) of neat energetic materials or propellant/explosive formulations using thermochemical codes. The "exact" method and three approximate techniques are described; the approximate techniques either eliminate the need to sum the internal energies of the predicted products, or eliminate the need to specify a freeze-out temperature. The various techniques are illustrated for HMX and a nitrocellulose/nitroglycerine (NC/NG) mixture.

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1. INTRODUCTION

Heat of explosion (HEX) is usually defined as the difference between the energies of formation of a material and the energies of formation of the explosion products (Meyer 1977). Experimentally, HEX is measured as the heat released when a material is ignited and burned in a bomb calorimeter in an inert atmosphere. The measurement is made after the products have cooled to near room temperature by noting the temperature rise of the calorimeter water jacket; HEX is calculated from this temperature rise using the effective heat capacity of the calorimeter body and water jacket. The experimentally determined HEX values include contributions due to cooling of the combustion products from the flame temperature (T_{fl}) to room temperature (T_r), and phase changes such as water condensation. These contributions are not generally available for use in gun and rocket propulsion, but, on the other hand, HEX is much easier to measure than impetus or specific impulse, and therefore is a convenient way of ranking the energy content of different formulations. Note that *heat of explosion* is a misnomer for two reasons: 1) many people consider the term "heat" to imply constant pressure enthalpy (H); an equally valid definition of this term is constant volume internal energy (U). Since a bomb calorimeter is a constant volume device, the latter usage of the term will be used in this report. 2) The sample usually undergoes combustion rather than explosion. In addition, the energetic materials community reports HEX values as positive numbers, even though exothermic energy release should be negative according to convention in the thermodynamics community. Strictly speaking then, HEX is defined in this report as the absolute value of the total energy released during constant volume combustion of a material in an inert atmosphere.

Measured HEX depend somewhat on conditions; in particular, HEX generally increases with increasing loading density, or with bomb prepressurization. To some extent, this is predicted thermodynamically, but there are other potential contributions: at lower loading densities or prepressurization levels, mixing with the cold gas initially present in the bomb calorimeter may quench some of the chemistry before it attains thermodynamic equilibrium, and/or mixing with the cold gas may raise the freeze-out temperature (T_{fo}) of the cooling combustion products. T_{fo} is the temperature during cooling at which the ratios of the various combustion products become invariant (Corner 1950), though phase changes may still occur.

It is increasingly of interest to be able to calculate HEX using a thermochemical code such as NASA-Lewis (Gordon and McBride 1976; Svehla and McBride 1973) or BLAKE (Freedman 1982). The "exact" method for calculating HEX with a thermodynamic code has been described elsewhere (Lenchitz et al. 1979) and will be summarized below. Since the exact method requires the T_{fo}, which is rarely known,

and since, in addition, it requires summing up the room temperature energies of the products using the mole fractions at T_{fo}, there is interest in approximate techniques which do not require knowledge of T_{fo}, and/or eliminate the need to make use of the composition of the combustion products. Three such approximate techniques are described below. They are illustrated for the case of CHNO chemistry, but may in fact be especially useful for chemistries involving other elements, where essentially nothing is known about T_{fo}. In addition to these three approximate techniques, which use general-purpose thermochemical codes, Baroody and Peters (1990) have described an approximate procedure employing a rocket motor code, where the chamber and exhaust conditions approximate the bomb calorimeter before and after cooling, respectively, and where corrections are applied to compensate for the fact that the rocket calculations are at constant pressure rather than constant volume.

HEX calculations are carried out on nitramines, cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) and cyclotetramethylene tetranitramine (HMX), as well a. a mixture of nitroglycerine (NG) and nitrocellulose (NC) at 12.6% nitration level. Thermochemical calculations were carried out using CET89, a recent version of the NASA-Lewis code (Gordon and McBride 1976; Svehla and McBride 1973) modified at the Army Research Laboratory (ARL) to run on a personal computer. All calculations were run on Intel 80386- and 80486-based PCs operating under MS-DOS. The procedures outlined in the following sections would be similar using other codes. In all cases, the goal is to calculate or estimate:

$$HEX = \Delta U_{r,298} = \left| U_{prod} - U_{react} \right| \quad (cal/g), \tag{1}$$

where ΔU_r is the change in energy at constant volume for the calorimetric reaction, and U_{prod} and U_{react} are the internal energies of the products and reactants, respectively, at room temperature (T_r = 25°C = 298.15 K). Analogous procedures could be used (using enthalpies instead of energies) for a constant pressure process. Table 1 lists values for the atomic make-up, molecular weight, and enthalpy of formation for the materials being studied.

2. ASSIGNMENT OF THE THERMODYNAMIC QUANTITIES H AND U.

The thermodynamic quantities H and U are the enthalpy and internal energy state functions for a given species. These quantities are related by the following equation:

$$H = U + PV, \tag{2}$$

Table 1. Selected Values for Materials Used in This Study

Material	C	H	N	O	MW (g/mol)	AH_f° (kcal/mol)
HMX	4	8	8	8	296.16	17.92
RDX	3	6	6	6	222.12	14.69
NC, 12.6% N	6	7.550	2.450	9.901	272.40	−169.20
NG	3	5	3	9	227.09	−88.60

where P is pressure and V is volume. Equation 2 can be modified to handle either gaseous or condensed species as follows. For gaseous species, the ideal gas equation of state,

$$PV = nRT, \tag{3}$$

may be combined with Equation 2 to give the following equation relating H and U:

$$H = U + nRT \quad \text{(gases)}, \tag{4}$$

where R is the gas constant, T is temperature, and n is the number of moles of gas involved. At room temperature, RT is equal to 592 cal/mol. In the case of condensed (liquid or solid) species, the PV product of Equation 2 is small enough that the following approximation may be made:

$$H \approx U \quad \text{(liquids, solids)}. \tag{5}$$

Equations 4 and 5 allow the assignment of internal energy in terms of the corresponding enthalpy.

Enthalpies are assigned *in the codes* by arbitrarily assuming $H^\circ_{298.15} = (\Delta H_f^\circ)_{298.15}$, where $(\Delta H_f^\circ)_{298.15}$ is the standard heat of formation (relative to the reference elements at 298.15 K and 0.1 MPa pressure) of the species of interest. Equation 5 then becomes

$$U \approx H^\circ_{298.15} \approx (\Delta H_f^\circ)_{298.15} \tag{6}$$

for liquids and solids, and Equation 4 becomes for gases. Since most energetic materials of interest exist

$$U = H^\circ_{298.15} - nRT \approx (\Delta H_f^\circ)_{298.15} - nRT \tag{7}$$

in condensed phases, Equation 6 is generally sufficient to assign the reactant energy (U) on the assigned thermodynamic scale. If gaseous product energies need to be assigned (e.g., see the exact calculation, below), then Equation 7 should be used.

A distinction needs to be made between the assigned quantity, U, and the energy of formation, ΔU_f. In Equations 6 and 7, U can be thought of as the internal energy of the product of a formation reaction (for the chemical species of interest) on the assigned energy scale; in other words, U represents an "absolute" energy on the scale defined by setting $H^o_{298.15} = (\Delta H^o_f)_{298.15}$. U differs from the energy of formation, ΔU_f, in that ΔU_f is defined as the difference of U for the formation species and the U's of the elemental constituents in their standard states; Kotlar (1992) presents a good discussion on the proper interpretation and assignment of internal energies. The use of the U's for the reactants and products in Equation 1 to calculate HEX is equivalent to the use of the corresponding ΔU_f's since the U contributions (to ΔU_f) from the elemental constituents would cancel out from the product and reactant internal energy terms. Often enthalpies of formation are more readily available than are energies of formation; this formalism for internal energy was chosen to simplify the calculations involved by using Equations 6 and 7.

3. HEX vs. HEAT OF COMBUSTION

The energy of combustion is experimentally measured through the use of a bomb calorimeter filled with an excess of oxygen. For a CHNO species, the combustion products would be liquid H_2O and gaseous CO_2 and N_2 according to the following equation (Cox and Pilcher, pp 54):

$$C_aH_bO_cN_d + (a + \frac{b}{4} - \frac{c}{2})\,O_2(g) \rightarrow aCO_2(g) + \frac{b}{2}H_2O(l) + \frac{d}{2}N_2(g). \qquad (8)$$

The measured energy of combustion, ΔU_c, can be converted to the enthalpy of combustion, ΔH_c, through the use of the following equation:

$$\Delta H_c = \Delta U_c + \Delta n_g RT, \qquad (9)$$

where Δn_g is the change in the number of moles of gas for the reaction and R is the gas constant; Equation 9 follows directly from Equation 4. When $C_aH_bO_cN_d$ exists entirely in the solid or liquid state, Δn_g takes on the value of (d/2 + c/2 – b/4). The enthalpy of combustion is typically used to calculate the enthalpy of formation for the compound being combusted.

HEX is measured in a similar manner as the heat of combustion except that the calorimeter is filled with an inert gas instead of oxygen. A simple calculation for estimating the enthalpy of explosion (ΔH_e) can be derived if one assumes that the only observed combustion species are CO, CO_2, H_2O(l), and N_2. This assumption excludes any consideration of O_2, H_2, or any fragmented species in the combustion products; the exclusion of H_2 is not unreasonable, since the water-gas equilibrium freeze-out temperature would typically be in the 1,500–1,800 K range (Ornellas 1966, 1968, 1974; Bernecker 1967), resulting in equilibrium constants which are unfavorable to the production of H_2 (Corner 1950; Meyer 1977). The explosion reaction is then approximated as:

$$C_aH_bO_cN_d \rightarrow (c - a - \frac{b}{2})CO_2(g) + (-c + 2a + \frac{b}{2})\,CO(g) + \frac{b}{2}\,H_2O(1) + \frac{d}{2}\,N_2(g). \quad (10)$$

Derivations of Equations 8 and 10 can be found in Appendix E.

The enthaply of combustion (ΔH_c) for Equation 8 can be expressed as:

$$\Delta H_c = a\Delta H_f[CO_2(g)] + \frac{b}{2}\,\Delta H_f[H_2O(l)] - \Delta H_f[C_aH_bO_cN_d]. \quad (11)$$

In a similar fashion, the enthalpy of explosion (ΔH_e) for Equation 10 can be expressed as:

$$\Delta H_e = (c - a - \frac{b}{2})\,\Delta H_f[CO_2(g)] + (-c + 2a - \frac{b}{2})\Delta H_f[CO(g)] + \frac{b}{2}\,\Delta H_f[H_2O(1)] - \Delta H_f[C_aH_bO_cN_d]. \quad (12)$$

Taking the difference between Equations 11 and 12, the following equation is obtained (solving for ΔH_e):

$$\Delta H_e = \Delta H_c + (\Delta H_f[CO(g)] - \Delta H_f[CO_2(g)])(2a + \frac{b}{2} - c). \quad (13)$$

By making the approximation HEX $\approx -\Delta H_e$, Equation 13 can be written (on a per gram basis) as:

$$HEX \approx \frac{(-\Delta H_c) - 67.63*(2a + 0.5b - c)}{MW}, \quad (14)$$

where ΔH_c is the enthalpy of combustion of the material in kcal/mol, MW is the molecular weight of the compound in g/mol, and the calculated HEX is in kcal/g. This particular approximation can be justified

by the fact that the reactions in Equations 8 and 10 would be expected to produce similar amounts of products in the gas phase; the $\Delta n_g RT$ terms in Equation 9 would roughly cancel out if the corresponding energies were used in place of the enthalpies in Equation 13. Typically, it is easier to find values for enthalpies of formation than for enthalpies of combustion. Where the enthalpy of combustion cannot be found for a given species, it may be calculated using Equation 11. Table 2 lists HEX values calculated using Equation 14 as well as literature values of HEX for HMX, RDX, NC, and NG. The enthalpy of combustion values listed in Table 2 were calculated using Equation 11 and are only listed for use in Equation 14. It should be noted that Equation 14 only applies in the case of pure compounds where the heat of combustion can be expressed on a molar basis. In the case of a multi-component formulation, Equation 14 could be used to generate *partial* HEX for each ingredient which could then be combined on a weight basis to estimate HEX for the formulation as a whole.

Table 2. HEX Values for Selected Energetic Materials Calculated Using Equation 14

Material	$-\Delta H_c$ (kcal/mol)	HEX		
		Eq. 14 (cal/g)	Literature (cal/g)	Reference
HMX	667.4	1,340	1,356	Lin and Chen 1986
RDX	501.8	1,346	1,370	Urbanski 1967
NC, 12.6% N	653.0	939	973	Urbanski 1965
NG	364.3	1,753	1,470	Urbanski 1965

4. COMPUTATIONAL METHODS USING THERMOCHEMICAL CODES

4.1 Exact Calculation of HEX. The following equation is based on the definition of HEX presented in Equation 1:

$$HEX = \left| \frac{\sum_{j=1}^{m} X_j U_j}{\sum_{j=1}^{m} X_j M_j} - \frac{\sum_{i=1}^{n} X_i U_i}{\sum_{i=1}^{n} X_i M_i} \right| \text{ (cal/g)}, \qquad (15)$$

where the m product mole fractions (X_j) in the first summation are those computed at the freeze-out temperature T_{fo}, the room temperature internal energies, U_j, are for the expected state following cooling to T_r (e.g., $H_2O(l)$), and division by the product molecular weights, M_j, gives HEX units of energy per unit weight (e.g., cal/g). For gaseous products, the U_j are related to the enthalpies of formation by Equation 7; the internal energies for use in the first term of Equation 15 are, therefore, obtained by subtracting RT (592 cal/mol) from the room temperature enthalpies of formation in the JANAF thermochemical tables (Chase et al. 1985). The second term in Equation 15 is simply the internal energy (cal/g) of the propellant or energetic material, obtained by summing the U_i for the n ingredients. For the usual case of a solid or liquid material, Equation 6 applies, so the enthalpies of formation can be used. Most thermochemical codes permit ingredient weight fractions to be input rather than mole fractions; most codes output the total energy of formation of the formulation, providing the second term in Equation 15 directly.

The exact procedure for calculating HEX has been described elsewhere (Lenchitz et al. 1979), and is briefly summarized as follows: If the code supports an assigned temperature and volume mode, as does the NASA-Lewis code, specify a volume (or loading density, ρ) and T, where an assumed T_{fo} is used for T, and run the code to produce the minimum energy (equilibrium) combustion product composition. For a CHNO formulation, the only significant products are usually CO, CO_2, H_2, $H_2O(g,l)$, N_2, CH_4, NH_3, and C(gr); where the methane, ammonia, and graphite result from oxygen deficiency in the energetic material or formulation. The predicted mole fractions at T_{fo} are then used, together with the molecular weights and room temperature internal energies to perform the summation in the first term of Equation 15. In the original implementation (Lenchitz et al. 1979), this was done by taking the product mole fractions at T_{fo} from the thermochemical code output, and inputting them into a small program running on a programmable calculator. More recently, we have done the summation by downloading the thermochemical code output into a spreadsheet (see Appendix A). Yet another procedure, for some thermochemical codes, is to enter the gas composition returned from the assigned temperature and volume calculation as input to an assigned energy and volume calculation, which is then run at T_r = 298.15 K; when specifying the composition, any gaseous H_2O should be condensed to liquid for the room temperature calculation. The final composition returned from the assigned energy and volume calculation is ignored, only making use of the output U for the mixture; since the calculation is run specifying constant U, the calculation is essentially a lazy way of summing up the internal energy of the input (T_{fo}) composition at room temperature. Of course, the ideal procedure is to modify the thermochemical code

to calculate a HEX automatically for one or more specified freeze-out temperatures. This modification has been implemented in a recent version of the BLAKE thermochemical code.

Table 3 shows calculated HEX for HMX and for a 60/40 mixture (by weight) of nitrocellulose (12.6% N)/nitroglycerine (NC/NG) using the exact procedure. The variation of HEX with loading density, ρ, is readily apparent in the data of Table 3, and is due to increased formation of C(gr), CH_4, and NH_3 with decreasing freeze-out temperature.

If a code does not support an assigned temperature and volume (or ρ) mode, the problem then becomes one of estimating the pressure at T_{fo} (i.e., the freeze-out pressure, P_{fo}) so that an assigned temperature and pressure calculation can then be carried out to find the composition at freeze out. The P_{fo} can be estimated from (Lenchitz et al. 1979):

$$P_{fo} = P_{fl}\left(\frac{T_{fo}}{T_{fl}}\right), \tag{16}$$

where T_{fl} and P_{fl} are the adiabatic flame temperature and pressure (i.e., the T and P before any cooling occurs). T_{fl} and P_{fl} are computed using an assigned energy and volume calculation. Equation 16 overestimates P_{fo} somewhat, since, in general, condensed species form at T_{fo}, and/or the average molecular weight of the gases increases on cooling to T_{fo}. This leads to the resulting HEX being a little too high; for typical CHNO propellants the error is usually only 20 cal/g or less (Lenchitz et al. 1979). This error can be eliminated by using an iterative procedure in place of Equation 16. This is done as follows. First, estimate P_{fo} from the ideal gas equation of state $P = \rho RT/M$ (for P in atm and ρ in g/cm^3, R = 82.06 cm^3-atm/mol-K) for the ρ and T_{fo} of interest, using a reasonable guess for the molecular weight M. Run the thermodynamic code at assigned temperature and pressure using this P and T. The resulting returned M is then used with the ideal gas equation of state to obtain an improved estimate of P_{fo}, this procedure being repeated until the computed ρ is within, say, 1% of the desired ρ. If the initial estimate of M is close, generally only two runs will be required; otherwise three should be sufficient to produce HEX identical to those with a code having the assigned temperature and volume option.

4.2 The $C_V dT$ Approximate Method. The first approximate method we will describe preserves the concept of a freeze-out temperature, while eliminating the need to sum up room temperature internal energies for the product species in equilibrium at T_{fo}. Starting from Equation 1, we have:

$$HEX = \left|U_{prod} - U_{react}\right| \approx \left|\left(U_{fo} - C_v\Delta T\right) - U_{react}\right|, \quad (17)$$

where C_v and U_{fo} are the specific heat and total internal energy of the product gases at T_{fo}, respectively,

Table 3. HEX (cal/g), Exact Calculation

	HMX[a] T_{fo} (K)				NC/NG[b] T_{fo} (K)			
ρ (g/cm^3)	900	1,100	1,300	1,500	900	1,100	1,300	1,500
0.01	1,504	1,382	1,356	1,356	1,408	1,291	1,278	1,278
0.05	1,540	1,445	1,372	1,357	1,447	1,341	1,284	1,279
0.10	1,549	1,469	1,393	1,361	1,457	1,365	1,295	1,280
0.20	1,556	1,491	1,419	1,371	1,464	1,391	1,315	1,283
0.50	1,562	1,517	1,454	1,398	1,470	1,421	1,347	1,297

[a] HMX: $U \approx \Delta H_f^\circ$ = + 17.92 kcal/mol = +60.52 cal/g.
[b] NC (12.6%N); $U \approx \Delta H_f^\circ$ = −169.2 kcal/mol = −621.0 cal/g.
NG: $U \approx \Delta H_f^\circ$ = −88.60 kcal/mol = 390.2 cal/g.
For 60% NC + 40% NG, U = −528.7 cal/g.

and $\Delta T = T_{fo} - 298.15$. Here, we are essentially approximating the internal energy of the products after cooling to room temperature by subtracting $C_v\Delta T$ from the internal energy output by the thermochemical code for the products at the freeze-out temperature: U_{fo} in Equation 17 is calculated from an assigned temperature and volume calculation run at a specified ρ and by setting $T = T_{fo}$. Since specific heat is actually a temperature-dependent quantity, an exact procedure would involve evaluation of $\int C_v dT$ rather than $C_v\Delta T$. Also, this approximation does not include the energy of phase changes such as water condensation. For typical CHNO formulations, the net result of these approximations is that the HEX are about 40 cal/g lower than for the exact method, as shown in Table 4. For HMX and NC/NG over a range of loading densities, simply adding 40 cal/g to the HEX from Equation 17 gives values that are within a fraction of a percent of those from the exact method described above.

Depending on the thermochemical code, some caution is required in determining the appropriate C_v to use in Equation 17. Many codes output only C_p, even for constant volume calculations. In this case, C_v can be estimated from:

Table 4. $C_v dT$ Method Approximate HEX (cal/g) and Percentage Difference from "Exact" Calculation (Table 3)

ρ (g/cm^3)	T_{fo} (K)			
	900	1,100	1,300	1,500
HMX				
0.01	1,452 (–3.42)	1,341 (–2.94)	1,317 (–2.90)	1,321 (–2.53)
0.05	1,483 (–3.72)	1,406 (–2.64)	1,333 (–2.82)	1,323 (–2.53)
0.10	1,491 (–3.79)	1,433 (–2.49)	1,356 (–2.66)	1,327 (–2.48)
0.20	1,496 (–3.84)	1,455 (–2.39)	1,384 (–2.44)	1,338 (–2.39)
0.50	1,501 (–3.89)	1,479 (–2.52)	1,423 (–2.12)	1,368 (–2.12)
HMX + 40 cal/g				
0.01	1,492 (–0.76)	1,381 (–0.05)	1,357 (0.04)	1,361 (0.42)
0.05	1,523 (–1.12)	1,446 (0.13)	1,373 (0.04)	1,363 (0.42)
0.10	1,531 (–1.21)	1,473 (0.23)	1,396 (0.22)	1.367 (0.46)
0.20	1,536 (–1.27)	1,495 (0.29)	1,424 (0.37)	1,378 (0.52)
0.50	1,541 (–1.33)	1,519 (0.12)	1,463 (0.63)	1,408 (0.74)
NC/NG				
0.01	1,353 (–3.89)	1,243 (–3.70)	1,231 (–3.68)	1,237 (–3.24)
0.05	1,386 (–4.21)	1,297 (–3.22)	1,238 (–3.60)	1,237 (–3.23)
0.10	1,394 (–4.30)	1,325 (–2.95)	1,251 (–3.45)	1,238 (–3.23)
0.20	1,400 (–4.36)	1,351 (–2.89)	1,273 (–3.17)	1,243 (–3.16)
0.50	1,405 (–4.42)	1,378 (–3.02)	1,310 (–2.70)	1,259 (–2.92)
NC/NG, + 40 cal/g				
0.01	1,393 (–1.05)	1,243 (–0.60)	1,271 (–0.55)	1,277 (–0.11)
0.05	1,426 (–1.45)	1,337 (–0.23)	1,278 (–0.49)	1,277 (–0.10)
0.10	1,434 (–1.55)	1,365 (–0.02)	1,291 (–0.36)	1,278 (–0.10)
0.20	1,440 (–1.63)	1,391 (–0.01)	1,313 (–0.13)	1,283 (–0.04)
0.50	1,445 (–1.70)	1,418 (–0.20)	1,350 (0.27)	1,299 (–0.17)

$$C_v = C_p - \left(\frac{R}{M}\right) \tag{18}$$

where M is the average molecular weight of the products. In the case of the NASA-Lewis code output, C_v can also be determined from:

$$C_v = \frac{-C_p}{\gamma_S \left(\frac{\partial \ln V}{\partial \ln P}\right)_T} \tag{19}$$

$(\partial \ln V/\partial \ln P)_T$ is the returned compressibility and γ_s is the isentropic gamma, which is generally within a few percent of $\gamma = C_p/C_v$. With the NASA-Lewis code, there are, however, additional complications: the C_p and γ_s returned by the code are equilibrium rather than frozen values, in that they include contributions due to shifting chemical equilibria in the combustion products. For propellants and explosives, it has been shown (Fifer and Cohen 1977) that for sufficiently high pressures and low loading densities, the equilibrium C_p may be considerably higher than the frozen C_p needed for the present calculation. The use of equilibrium rather than frozen properties will result in anomalously high HEX. The safest way to preclude this potential problem when using NASA-Lewis is to request that transport values also be returned; this results in frozen specific heats being returned, resulting in HEX values similar to those determined using codes that output only frozen parameters. In this case, only Equation 18 should be used to calculate a frozen C_p; under frozen conditions, Equation 19 reduces to $C_v = C_p/\gamma$, where γ is not explicitly calculated by the code. Note, however, that for systems which produce condensed products, the returned transport properties (including C_p) are for the gas phase only; in addition, the M returned by the NASA-Lewis code (for use in Equation 18) is not a true average molecular weight, but rather corresponds to a quantity defined by total weight (both gaseous and condensed) divided by the moles of gas only. A sample calculation for this method which makes use of Equation 18 is presented in Appendix B of this report. When dealing with systems that produce significant amounts of condensed products, it is recommended to either use a code (other than NASA-Lewis) which returns true average molecular weights or use a different approximate method.

4.3 The Room Temperature Method. This is the first of two methods that not only do not require weighted summation of product internal energies (Equation 15), but, in addition, do not require freeze-out temperatures to be specified. Such approximate methods are particularly appropriate for chemistries or calorimetric conditions where there is little information about the freeze-out temperature(s).

In the room temperature approximate method, it is assumed that there is no freeze-out of chemistry on cooling of the product to T_r. This is equivalent to saying that $T_{fo} = T_r = 298.15$ K. To do the calculation, an assigned temperature and volume (or density) calculation is carried out for the desired loading densities, specifying T = 298.15. From the returned U_{prod} for the combustion products at 298.15 K, U_{react} is subtracted (Equation 1) to give HEX (see Appendix C for an example calculation). In using this method, we usually restricted the products to CO, CO_2, H_2, N_2, H_2O, and H_2O(l), since otherwise at this low temperature unrealistically large amounts of C(gr), CH_4, NH_3, and other products are predicted. As shown in Table 5, it is then found that the computed HEX are virtually independent of loading density for CHNO systems, with HEX = 1,355 cal/g for HMX and 1,278 cal/g for NC/NG. The HEX are similar to those calculated in the exact method with a high (e.g., 1,500 K) rather than low (e.g., 900 K) T_{fo}. This results primarily from the exclusion of C(gr), CH_4, and NH_3, and to a much smaller extent, from alteration of the water-gas equilibrium ($CO + H_2O \rightleftharpoons CO_2 + H_2$) due to formation of H_2O(l) at equilibrium. Allowing all species, the HEX increases to about 1,630 cal/g for HMX, and about 1,524 cal/g for NC/NG. As in the exact and $C_v dT$ approximate methods, a dummy assigned energy and volume calculation can be used, if desired, to calculate U_{react} from the energies of formation for the separate ingredients and an assigned temperature and pressure calculation can be used, with estimated P, to obtain the product U_{prod} if the code does not offer the assigned temperature and volume mode. For CHNO chemistry with CH_4, NH_3, and C(gr) excluded, the density- (pressure-) independence of the computed U_{prod} means that an accurate estimate of P is not necessary, so no iterations are required.

4.4 The Inert Diluent Method. The other approximate method that avoids both the summation of Equation 15 and the need to specify T_{fo} is the inert diluent method. In this method, a large excess of inert gas (e.g., Argon) is added to the energetic material, and an assigned energy and volume (or density) calculation run. The effect of the diluent is to provide a heat sink for the reaction exothermicity, resulting in computed adiabatic flame temperatures that are only a few degrees above room temperature. HEX is determined using the following equation:

$$HEX = \left|U_{prod} - U_{react}\right| = N\int C_v dT \approx \frac{NC_p\Delta T}{\gamma}, \qquad (20)$$

where ΔT is the computed temperature rise ($T_{fl} - T_{initial}$), N is the reciprocal of the weight fraction of propellant or explosive in the mixture, and C_p and γ are as have been previously defined. The small ΔT serves three purposes: a) it allows condensables to condense, as in the calorimeter; b) it reduces the error associated with assuming a constant specific heat; and c) for the NASA-Lewis code, the low T_{fl} makes

it less likely that the C_p will be too large due to equilibrium reaction effects, although in some cases, phase equilibria could result in equilibrium C_p being larger than the frozen ones. Unlike all of the other methods described above, this method does not require the explicit subtraction of U_{react} from an approximation to U_{prod}, but instead evaluates HEX according to the right-hand side of Equation 20. An example calculation for this method is presented in Appendix D. As for the room temperature method, it is necessary to exclude many species that would otherwise be predicted in unreasonable amounts, including CH_4, NH_3, and C(gr), and, as for the room temperature method, this results in HEX values that are almost totally independent of loading density.

Table 5. Summary of All Methods for HEX (cal/g) at Selected Conditions

T_{fo}(K)	"Exact"		"CvdT + 40"		"Room T" No. Species		"Inert Diluent" No. Species		Equation 14[b,d]	Lit.[c,d]
ρ (g/cm^3)	900 K	1,500 K	900 K	1,500 K	6	all	6 + Ar	all		
HMX										
0.01	1,504	1,356	1,492	1,361	1,354	1,629	1,355	1,495	1,340	1,356
0.05	1,540	1,357	1,523	1,363	1,355	1,630	1,355	1,495	1,340	1,356
0.10	1,549	1,361	1,531	1,367	1,355	1,630	1,355	1,495	1,340	1,356
0.20	1,555	1,371	1,536	1,378	1,355	1,630	1,355	1,495	1,340	1,356
0.50	1,562	1,398	1,541	1,408	1,355	1,630	1,355	1,632[a]	1,340	1,356
NC/NG										
0.01	1,408	1,278	1,393	1,277	1,276	1,522	1,271	1,397	1,265	—
0.05	1,447	1,279	1,426	1,277	1,277	1,523	1,271	1,397	1,265	—
0.10	1,457	1,280	1,434	1,278	1,278	1,524	1,271	1,397	1,265	—
0.20	1,464	1,283	1,440	1,283	1,278	1,524	1,271	1,397	1,265	—
0.50	1,470	1,297	1,445	1,299	1,278	1,524	1,271	1,519[a]	1,265	—

[a] H_2O (l) appears at this and higher ρ.
[b] From Table 2. Values for NC/NG are calculated by taking 60% HEX_{NC} + 40% HEX_{NG} calculated using Equation 14. HEX_{NC} = 1,753 cal/g.
[c] No loading density was given for the literature value for HMX (Table 2).
[d] It is not intended to imply that these values are independent of loading density.

A convenient diluent is Argon. Using 1 part formulation + 999 parts (by weight) of Argon (N = 1000), the ΔT is typically 20–22 K. For sufficient accuracy, it is necessary to have the code output T_{fl} to ±0.1, or preferably ±0.01 K. Less diluent (e.g., N = 100) can be used if the source code is not available to make this format modification. Using 999 parts of Argon, and allowing only CO, CO_2, H_2,

N_2, H_2O, and H_2O(l) to form, Equation 20 gives HEX values of 1,355 cal/g for HMX, and 1,271 cal/g for NC/NG. For HMX, as shown in Table 5, this value is identical to that using the room temperature method; for NC/NG, it is seven cal/g less. If all species are allowed, HEX values for HMX are about 140 cal/g higher, and for NC/NG about 126 cal/g higher, but unrealistically high amounts of graphite (e.g., 20–30 mol %) are predicted. With all species allowed and 999 parts Argon, there is a sudden additional increase of 122 (NC/NG) to 137 (HMX) cal/g in going from $\rho = 0.2$ to $\rho = 0.5$ g/cm^3; this is due to the appearance of H_2O(l) at this loading density. Of course, H_2O(l) would appear at much lower loading densities if it were not for the Argon diluent. This points out the value of running the code for extremely high loading densities (e.g., $\rho = 10$ or 100 g/cm^3); although these are unachievably high loading densities, they force the water to condense as it would in the absence of the inert diluent.

With the inert diluent method, it is also possible to shift the ratios of predicted combustion products by using one of the combustion products as the (not exactly inert) diluent. For example, for HMX, using CO_2 as the diluent increases CO somewhat, lowering HEX 7 cal/g compared to Argon, using CO as diluent (N = 700) suppresses all water formation (HEX unchanged), using H_2O as diluent (N = 500, H_2O(l) not allowed) suppresses all CO (HEX increased 1 cal/g), and using H_2 as diluent (N = 50 due to much lower C_p for H_2) causes more H_2O(l) to form and increases CO/CO_2, causing HEX to decrease by 12 to 28 cal/g depending on ρ. While these changes are small due to the low ΔU for the water gas ($CO + H_2O \rightleftharpoons CO_2 + H_2$) reaction, for other chemistries, use of a combustion product as diluent may in some cases help force a better match between predicted products and those recovered from the calorimeter, producing a better match between experimental and theoretical HEX.

5. SUMMARY

Three approximate methods to estimate HEX for energetic materials using a standard thermochemical code have been outlined. The results of these methods have been compared to those obtained using the exact method for calculating HEX at a given freeze-out temperature. One of these methods requires the use of a freeze-out temperature while the other two do not. The three approximate methods and the exact method are reviewed below.

The exact method is based on running an assigned temperature and volume calculation at an assumed freeze-out temperature. The calculated product composition (at T_{fo}) is used to calculate a room temperature internal energy based on the room temperature internal energies for the product species. Any

gaseous water is converted to liquid water prior to calculating the internal energy of the combustion products. HEX is calculated by subtracting the internal energy of the uncombusted material from that of its combustion products.

The $C_v dT$ approximate method is also based on running an assigned temperature and volume calculation at an assumed freeze-out temperature. This method avoids the summation of combustion product internal energies by subtracting the quantity $C_v \Delta T$ from the calculated internal energy at the freeze-out temperature to get the approximate internal energy of the combustion products at room temperature. As in the exact method, HEX is calculated by subtracting the internal energy of the uncombusted material from that of its combustion products. The ΔT is $T_{fo} - 298.15$ K and the C_v is the constant volume heat capacity, either returned by the code or calculated as a derived quantity from other values returned by the code. One needs to be careful to choose a code that can handle condensed species if they are produced. For the CHNO chemistries looked at in this report, HEX values calculated were about 40 cal/g lower than those using the exact method.

The room temperature method requires no preassigned freeze-out temperature, and like the $C_v dT$ approximate method, avoids the summation of combustion product internal energies. As is the case with the exact method and the $C_v dT$ approximate method, this method is based on an assigned temperature and volume calculation, but unlike these other two methods, the calculation is run at 298.15 K. The combustion product internal energy is calculated directly from the code, and HEX is determined by subtracting the internal energy of the uncombusted material from that of its combustion products. There is a need to restrict the permissable product species when using this method to prevent excess formation of C(gr), CH_4, NH_3, and similar combustion products in the code. The calculated HEX is virtually independent of loading density when this method is used.

The inert diluent method, like the room temperature method requires no assumed freeze-out temperature and also avoids the summation of combustion product internal energies. In this method, a large excess of inert gas (e.g., Argon) is added to the energetic material and an assigned energy and volume calculation is run. The effect of the diluent is to limit the temperature rise to a few tens of degrees. HEX is determined using a few quantities reported by the code without the need to subtract U_{react} from an approximation to U_{prod}. As with the room temperature method, there is a need to omit species such as C(gr), CH_4, and NH_3, and the calculated HEX values are almost totally independent of loading density. Due to the small temperature rise, the code is required to output temperature to ±0.1 K

or ±0.01 K. Water can be forced to condense out using large loading densities of 10 or 100 g/cm^3, but since HEX is relatively unaffected by loading density, this does not make a large difference.

Since two of the approximate techniques (room temperature and inert diluent) eliminate the need to specify a composition freeze-out temperature, these may be appropriate for situations where T_{fo} is unknown, especially in cases which cannot be described by simple CHNO chemistry (such as metallized propellants or pyrotechnics). It is interesting to note that these two methods give similar values which seem to be quite independent of loading density if the number of product species allowed is kept small.

4. REFERENCES

Baroody, E. E., and S. T. Peters. "Heat of Explosion, Heat of Detonation, and Reaction Products: Their Estimation and Relation to the First Law of Thermodynamics." NOSIH Report IHTR 1340, March 1990.

Bernecker, R. R., and L. C. Smith. "On the Products Formed in the Combustion of Explosives. Freeze-out of the Water-Gas Reaction." Journal of Physical Chemistry, vol. 71, pp. 2381–2389, 1967.

Chase, M. W. Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud. "JANAF Thermochemical Tables. Third Edition." Journal of Physical Chemistry Reference Data, vol. 14, Supplement 1 (2 volumes), 1985.

Corner, J. Theory of the Interior Ballistics of Guns, Chapter 3, New York: John Wiley and Sons, Inc., 1950.

Cox, J. D., and G. Pilcher. Thermochemistry of Organic and Organometallic Compounds, London: Academic Press, 1970.

CPIA. Solid Propellant Ingredients Manual, Chemical Propulsion Information Agency/M3, April 1987.

Fifer, R. A., and A. Cohen. "High Temperature Thermal Conductivity and Heat Transfer in Gun Propellant and Primer Combustion Gases." Proceedings of the 14th JANNAF Combustion Meeting, CPIA Publication 292, vol. II, pp. 363–387, December 1977.

Freedman, E. "BLAKE - A Thermodynamics Code Based on Tiger: User's Guide and Manual." ARBRL-TR-02411, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, July 1982.

Gordon, S., and B. J. McBride. "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations." NASA SP-273, March 1976.

Kotlar, A. J. "The Proper Interpretation of the Internal Energy of Formation used in Thermodynamic Equilibrium Calculations." BRL-MR-3985, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD, July 1992.

Lenchitz, C., L. A. Bottei, E. Hayes, B. Haywood, and R. A. Fifer. "Anomalies in Nitramine Propellant Combustion." Proceedings of the 16th JANNAF Combustion Meeting, CPIA Publication 308, vol. III, pp. 309–329, December 1979.

Lin, K., and S. I. Chen. "The Effects of Particle Size on Heat of Explosion." Analysis of Propellants and Explosives - Chemical and Physical Methods. Seventeenth International Annual Conference of ICT, pp. 78/1-11. Fraunhofer-Institüt füt Treib- und Explosivestoffe, Karlsruhe, Germany, 25-27 June 1986.

Meyer, R. Explosives. Verlag Chemie, Weinheim, 1977.

Ornellas, D. L. "The Heat and Products of Detonation of Cyclotatramethylenetetranitramine, 2,4,6-Trinitrotoluene, Nitromethane, and Bis[2,2-dinitro-2-fluoroethyl]formal." Journal of Physical Chemistry, vol. 72, pp. 2390-2394, 1968.

Ornellas, D. L. "The Heat and Products of Detonation in a Calorimeter of CHO, HNO,CHNF, CHNO, CHNOF, and CHNOSi Explosives." Combustion and Flame, vol. 23, pp. 37–46, 1974.

Ornellas, D. L, J. H. Carpenter, and S. R. Gunn. "Detonation Calorimeter and Results Obtained with Pentaerythritol Tetranitrate (PETN)." Rev. Sci. Instr., vol. 37, pp. 907–912, 1966.

Svehla, R. A., and B. J. McBride. "Fortran IV Computer Program for Calculation of Thermodynamic and Transport Properties of Complex Chemical Systems." NASA TN D-7056, January 1973.

Urbanski, T. Chemistry and Technology of Explosives, vol. 2, pp. 52 and 312. Oxford: Pergamon Press, 1965.

Urbanski, T. Chemistry and Technology of Explosives, vol. 3, p. 84, Oxford: Pergamon Press, 1967.

APPENDIX A:

EXAMPLE OF THE EXACT METHOD FOR HMX, T_{fo} = 900 K, LOADING DENSITY OF 0.1 g/cm^3

INTENTIONALLY LEFT BLANK.

Start by running an assigned temperature and volume (TV = T) calculation at the desired freeze-out temperature and loading density. The input file looks as follows:

```
REACTANTS
C 4.      H 8.      N 8.      O 8.          .          1.0      17924.5S 298.15      HMX

NAMELISTS
 &INPT2 TV=T,RHO=0.1,T=900,TRACE=1.E-03/
```

The following calculated values are extracted from the output file:

```
 THERMODYNAMIC PROPERTIES

 P, ATM                254.55
 T, DEG K              900.00
 RHO, G/CC           1.0000-1
 H, CAL/G            -1198.13
 U, CAL/G            -1259.77
 G, CAL/G            -2695.48
 S, CAL/(G)(K)         1.6637

 M, MOL WT             29.013
 (DLV/DLP)T          -1.01010
 (DLV/DLT)P            1.1610
 CP, CAL/(G)(K)         .5522
 GAMMA (S)             1.1864
 SON VEL,M/SEC          553.2
 IMPETUS (J/G)          257.9

MOLE FRACTIONS

CH4                 6.0821-2  <==
CO                  1.2956-2  <==
CO2                 2.5527-1  <==
H2                  2.6358-2  <==
H2O                 2.2487-1  <==
NH3                 8.5717-4  <==
N2                  3.7375-1  <==
C(GR)               4.5115-2  <==
```

The calculated mole fractions, heats of formation, and molecular weights are loaded into a spreadsheet to calculate the internal energy (at 298.15 K) of the combustion products for the equilibrium composition calculated at the freeze-out temperature. All water is forced to condense out (the heat of formation for liquid water should be used).

Species	Heat of Formation (kJ/mole)	Heat of Formation (kcal/mole)	-RT	U(298.15 K) (kcal/mole)
CH4	-74.873	-17.895	-0.592	-18.487
CO	-110.527	-26.417	-0.592	-27.009
CO2	-393.522	-94.054	-0.592	-94.646
H2	0.000	0.000	-0.592	-0.592
H2O(L)	-285.830	-68.315		-68.315
NH3	-45.898	-10.970	-0.592	-11.562
N2	0.000	0.000	-0.592	-0.592
C(GR)	0.000	0.000		0.000

Species	X	M	U (cal/mole)	X*U	X*M
CH4	6.0821E-02	16.043	-18487	-1124.4	0.9757
CO	1.2956E-02	28.010	-27009	-349.9	0.3629
CO2	2.5527E-01	44.010	-94646	-24160.3	11.2344
H2	2.6358E-02	2.016	-592	-15.6	0.0531
H2O(L)	2.2487E-01	18.015	-68315	-15362.0	4.0511
NH3	8.5717E-04	17.031	-11562	-9.9	0.0146
N2	3.7375E-01	28.013	-592	-221.3	10.4700
C(GR)	4.5115E-02	12.011	0	0.0	0.5419
			Summations	-41243.4	27.7037

Sum(X*U)/Sum(X*M) -1488.73 cal/g

The calculated value of −1,488.73 cal/g is the internal energy of the combustion products at 298.15 K (using the freeze-out composition). The internal energy of the uncombusted HMX is subtracted from this value to determine HEX:

HEX = |-1488.73 - + 60.52| = 1549 cal/g

APPENDIX B:

EXAMPLE OF $C_v dT$ APPROXIMATE METHOD FOR HMX, T_{fo} = 900 K, LOADING DENSITY OF 0.1 g/cm^3

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Start by running an assigned temperature and volume (TV = T) calculation with transport properties (TRNSPT = T) at the desired freeze-out temperature (900 K) and loading density (0.1 g/cm^3). The input file looks as follows:

```
REACTANTS
C 4.     H 8.     N 8.     O 8.        .        1.0     17924.5S 298.15     HMX

NAMELISTS
 &INPT2 TV=T,TRNSPT=T,T=900,RHO=0.1,TRACE=1.E-03/
```

The following calculated values are extracted from the output file:

```
 THERMODYNAMIC PROPERTIES

 P, ATM              254.55
 T, DEG K            900.00
 RHO, G/CC         1.0000-1
 H, CAL/G          -1198.13
 U, CAL/G          -1259.77  <==
 G, CAL/G          -2695.48
 S, CAL/(G)(K)       1.6637

 M, MOL WT           29.013  <==
 (DLV/DLP)T        -1.01010
 (DLV/DLT)P          1.1610
 CP, CAL/(G)(K)       .5522
 GAMMA (S)           1.1864
 SON VEL,M/SEC        553.2
 IMPETUS (J/G)        257.9

 TRANSPORT PROPERTIES (GASES ONLY)
   CONDUCTIVITY IN UNITS OF MILLICALORIES/(CM)(K)(SEC)

 VISC,MILLIPOISE    .37253

  WITH EQUILIBRIUM REACTIONS

 CP, CAL/(G)(K)     12.6465
 CONDUCITVITY         .3880
 PRANDTL NUMBER     12.1432

  WITH FROZEN REACTIONS

 CP, CAL/(G)(K)       .3514  <==
 CONDUCITVITY         .1781
 PRANDTL NUMBER       .7349
```

The mole fractions for this calculation are the same as those in Appendix A and are not reproduced here. The amount of graphite produced is small enough to warrant running this calculation with the NASA-Lewis code. C_v is calculated according to Equation 18 using the C_p returned in the transport properties calculation with frozen reactions (.3514 cal/g-K), M (29.013 g/mol), and R (1.987 cal/mol-K). ΔT is the difference between T_{fo} and 298.15 K:

$$C_v = .3514 - 1.987/29.013 = 0.2829 \text{ cal/g-K}$$

$\Delta T = 900 - 289.15 = 601.85$ K

$C_v\Delta T = 170.27$ cal/g

The calculated internal energy of the combustion products is the difference between U calculated at T_{fo} and $C_v\Delta T$:

$U_{298.15} = -1259.77 - 170.27 = -1430.04$ cal/g

The internal energy of the uncombusted HMX is subtracted from this value to determine HEX. A correction of 40 cal/g is added to this value for the CHNO chemistries looked at in this report:

$HEX = |-1430.04 - +60.51| = 1491$ cal/g

$HEX + 40 = 1491 + 40 = 1531$ cal/g

APPENDIX C:

EXAMPLE OF ROOM TEMPERATURE METHOD FOR HMX AT A LOADING DENSITY OF 0.1 g/cm^3

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Prior to running this method, the thermo library could be restricted to CO, CO_2, H_2, N_2, H_2O, and H_2O(l) to eliminate the prediction of unrealistically large amounts of C(gr), CH_4, and NH_3. Run an assigned temperature and volume (TV = T) calculation at room temperature. The input file looks as follows:

```
REACTANTS
C 4.      H 8.      N 8.      O 8.          .          1.0      17924.5S 298.15      HMX

NAMELISTS
 &INPT2 TV=T,T=298.15,RHO=0.1,TRACE=1.E-03/
```

The following calculated values are extracted from the output file:

```
 THERMODYNAMIC PROPERTIES

 P, ATM                98.833
 T, DEG K              298.15
 RHO, G/CC           1.0000-1
 H, CAL/G            -1270.23
 U, CAL/G            -1294.17   <==
 G, CAL/G            -1702.13
 S, CAL/(G)(K)         1.4486

 M, MOL WT             24.755
 (DLV/DLP)T          -1.00361
 (DLV/DLT)P            1.0094
 CP, CAL/(G)(K)         .3166
 GAMMA (S)             1.3419
 SON VEL,M/SEC          366.6
 IMPETUS (J/G)          100.1


 MOLE FRACTIONS

 CO                  3.3352-3
 CO2                 3.3000-1
 H2                  3.3000-1
 H2O                   .00031
 N2                  3.3333-1
 H2O(L)              3.0218-3
```

Since the calculation is run at room temperature, it is a simple matter to subtract the internal energy of the uncombusted HMX from the calculated U to get HEX:

```
HEX = |-1294.17 - +60.51| = 1355 cal/g
```

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APPENDIX D:

EXAMPLE OF THE INERT DILUENT METHOD FOR HMX AT A LOADING DENSITY OF 0.1 g/cm^3

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Prior to running this method, the thermo library could be restricted to CO, CO_2, H_2, N_2, H_2O, H_2O(l), and Argon. Run an assigned energy and volume (UV = T) calculation specifying the energetic material (or formulation) and Argon. The following example will use 1 part HMX to 999 parts Argon by weight. The input file looks as follows:

```
REACTANTS
C 4.      H 8.      N 8.      O 8.        .          1.0      17924.5S 298.15      HMX
AR1.         .         .         .        .        999.0       -592.5G 298.15

NAMELISTS
 &INPT2 UV=T,RHO=0.1,TRACE=1.E-07/
```

The following calculated values are extracted from the output file:

```
 THERMODYNAMIC PROPERTIES

 P, ATM                65.003
 T, DEG K              316.26   <==
 RHO, G/CC           1.0000-1
 H, CAL/G               .98551
 U, CAL/G             -14.756
 G, CAL/G             -228.88
 S, CAL/(G)(K)          .7268

 M, MOL WT             39.923
 (DLV/DLP)T          -1.00000
 (DLV/DLT)P            1.0000
 CP, CAL/(G)(K)         .1246   <==
 GAMMA (S)             1.6656   <==
 SON VEL,M/SEC          331.2
 IMPETUS (J/G)           65.9


 MOLE FRACTIONS

 AR                  9.9838-1
 CO                  2.6729-6
 CO2                 5.3655-4
 H2                  5.3655-4
 H2O                 2.6729-6
 N2                  5.3922-4
```

HEX is calculated directly from Equation 20 (N = 1000):

```
HEX = 1000*0.1246*(316.26-298.15)/1.6656 = 1355 cal/g
```

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APPENDIX E:

DERIVATION OF EQUATIONS FOR BOMB CALORIMETER COMBUSTION AND EXPLOSION REACTIONS

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This Appendix details how the molecular coefficients in Equations 8 and 10 in the body of this report were obtained. Combustion of a $C_aH_bO_cN_d$ compound in an excess of O_2 would be expected to go to completion and yield CO_2, H_2O, and N_2, along with any unreacted O_2. For this combustion reaction, and neglecting the excess O_2, start with the following unbalanced chemical equation:

$$C_aH_bO_cN_d + wO_2 \rightarrow xCO_2 + yH_2O + zN_2. \qquad \text{(E-1)}$$

The coefficients x, y, and z in Equation E-1 are easily determined from the a, b, and d coefficients since C, H, and N each appear once on the right side of the equation: $z = d/2$, $y = b/2$, and $x = a$. Equation E-1 now becomes:

$$C_aH_bO_cN_d + wO_2 \rightarrow aCO_2 + \frac{b}{2}H_2O + \frac{d}{2}N_2. \qquad \text{(E-2)}$$

The O_2 coefficient, w, can now be solved for in terms of the coefficients for those species which contain oxygen. If the coefficents are put in terms of O_2, or two atomic oxygen equivalents, the following equation can be used to solve for w:

$$\frac{c}{2} + w = a + \frac{b}{4}, \qquad \text{(E-3)}$$

where c/2 comes from $C_aH_bO_cN_d$, w is the coefficient for O_2, a is the coefficient for CO_2, and b/4 is one-half the coefficient for H_2O. Equation E-3 is easily solved for w. Making the substitution for w in Equation E-2 yields Equation 8:

$$C_aH_bO_cN_d + (a + \frac{b}{4} - \frac{c}{2})O_2 \rightarrow aCO_2 + \frac{b}{2}H_2O + \frac{d}{2}N_2. \qquad \text{(E-4)}$$

Equation 10 can be derived in a similar manner. The explosion process here is treated as an incomplete combustion, since the reaction proceeds under an inert environment such as Ar or N_2. In this case, only H_2O, CO_2, N_2, and CO, will be considered as combustion products. The explosion reaction can now be written in an unbalanced form as:

$$C_aH_bO_cN_d \rightarrow wCO_2 + xCO + yH_2O + zN_2. \qquad \text{(E-5)}$$

The H_2O and N_2 coefficients are determined in exactly the same way as was the case for the combustion reaction above: y = b/2, z = d/2. This leaves the CO_2 and CO coefficients, w and x, which can be determined from the a, b, and c coefficients. The partially balanced reaction looks like

$$C_aH_bO_cN_d \rightarrow wCO_2 + xCO + \frac{b}{2}H_2O + \frac{d}{2}N_2. \qquad \text{(E-6)}$$

The following two equations are set up to conserve the C and O mass balance:

$$C: \quad a = w + x \qquad \text{(E-7)}$$

$$O: \quad c = 2w + x + \frac{b}{2}, \qquad \text{(E-8)}$$

where the coefficients a and c in Equation E-7 and E-8 come from $C_aH_bO_cN_d$, the w, x, and b coefficients come from CO_2, CO, and H_2O, respectively, and the O mass balance in Equation E-8 is based on one atomic oxygen equivalent. One can solve for w by subtracting Equation E-7 from Equation E-8. It is then a simple matter to make the substitution for w in Equation E-7 to solve for x:

$$w = c - a - \frac{b}{2} \qquad \text{(E-9)}$$

$$x = -c + 2a + \frac{b}{2}. \qquad \text{(E-10)}$$

Making the substitutions for w and x in Equation E-6 yields Equation 10:

$$C_aH_bO_cN_d \rightarrow (c - a - \frac{b}{2})CO_2 + (-c + 2a + \frac{b}{2})CO + \frac{b}{2}H_2O + \frac{d}{2}N_2. \qquad \text{(E-11)}$$

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